Indian J. Phys. **76A** (4), 369-372 (2002)

IJP A
— an international journal

D. C. electrical conductivity measurements on KDP single crystals added with NaCl and NaBr

G Deepa, T H Freeda and C Mahadevan*
Physics Research Centre, S. T. Hindu College,
Nagercoil - 629 002, Tamilnadu, India

E-mail mahad@sancharnet.in

Received 30 January 2002, accepted 18 April 2002

Abstract : Pure and impurity added (with NaCl and NaBr) KDP (potassium dihydrogen orthophosphate) single crystals were grown by the slow evaporation method from aqueous solutions. Density was measured by the flotation method. D.C. electrical conductivity measurements were carried out along both the unique axis and perpendicular directions at various temperatures ranging from 40 to 150°C by the conventional two probe method. The present study shows that the conductivity in KDP crystals, for both the impurities considered, increases with the increase in temperature. Also, the impurity addition reduced the conductivity. However, no systematic variation was observed with impurity concentration. Activation energies were also determined and reported.

Keywords : Impurity added KDP crystals, electrical conductivity, activation energy

PACS Nos. : 61.72.Ss, 72.15.Eb, 77.84.Fa

1. Introduction

Crystal growth and characterization is an expanding field in materials science which is identified as a thrust area of research. Artificial crystals are grown everyday and now we are more concerned to discover new materials for the purpose of industrial and academic uses. Due to the increased need of crystals in solid state devices, scientists' interests have turned from pure crystals to mixed and impurity added (doped) crystals (controlled mixing and controlled impurity addition).

Potassium dihydrogen orthophosphate (KDP), KH_2PO_4, is an interesting material both academically and industrially. Several research workers have shown considerable interest on it [1-8]. KDP crystals belong to the scalenohedral (twelve sided polyhedron) class of tetragonal crystal system at room temperature. The room temperature paraelectric phase of KDP has a tetramolecular unit cell having the dimensions given as $a = b = 7.448$Å and $c = 6.977$Å [9].

Aiming at discovering new materials, a research programme is being carried out in this laboratory on the growth and physical properties of pure and impurity added KDP crystals. As a part of the programme, we have studied the effect of different kinds of impurities [both organic and inorganic (having common anion or cation and no common ion with KDP)] added heavily (impurity added in the KDP solution used for the growth of crystals with impurity concentration ranging from 2000 to 10000ppm, *i.e.* 0.2 to 1.0 mole%) on the D.C. electrical conductivity at various temperatures ranging from room temperature (minimum) to 150°C (maximum) of KDP crystals grown by both the slow evaporation and gel methods. We have already reported the results of our studies on KDP added with some ammonium compounds, *viz.* NH_4Cl, NH_4NO_3, $NH_4H_2PO_4$, $(NH_4)_2SO_4$ [10]; potassium compounds, *viz.* KCl and KNO_3 [11]; organic compounds, *viz.* urea and thiourea [12]; *etc.* Herein, we report the results of our study on KDP added with sodium halides, *viz.* NaCl and NaBr (ionic conductors having no common ion with KDP).

2. Experimental details

Analytical reagent grade (AR) samples of KH_2PO_4, NaCl and NaBr along with double distilled water were used for the growth of single crystals by slow evaporation method. KDP

* Corresponding Author

was added with NaCl and NaBr separately each in six different KDP: impurity molecular ratios, *viz.* 1:0.000 (pure KDP), 1:0.002, 1:0.004, 1:0.006, 1:0.0008 and 1:0.010. The impurity was dissolved in 2.5M solution of KDP. Supersaturated aqueous solution of the salt (2.5M) was prepared in a 100ml beaker (corning glass vessel) and allowed to equilibrate at the desired temperature. The crystals were grown in the unstirred condition. The temperature and volume were kept constant respectively at 30°C and 20ml for all the crystal growth experiments. Small crystals appeared in the beginning due to slow evaporation and grew larger in considerable finite time. Best crystals were selected from this and used for the measurements.

In order to understand qualitatively whether the added impurity has entered into the KDP lattice or not, we carried out the density measurements by using the flotation technique. Carbon tetrachloride of density 1.594 g/cc and bromoform of density 2.890 g/cc are respectively, the rarer and denser liquids used.

As it was difficult to determine the impurity concentration in the crystal without using sophisticated techniques, no experiment was carried out to determine this. However, we followed an approximate method available in the literature [13] to do the same.

If X and Y are the initial concentrations (g/100cc) of A and B, the final stoichiometry will be $(X-A_1):(Y-A_2)$, where A_1 and A_2 are the solubilities of components A and B, respectively. If we simply use this relation, in the present study, we would get negative value for $(Y-A_2)$. So in order to avoid this situation, we modified the above ratio as

$$(10000X - A_1):(10000Y - A_2).$$

The values obtained are expected to be reasonable ones and any inaccuracy if present, will be negligible.

Crystals with high transparency and large defect-free size (>3mm) were selected and used for the D.C. electrical conductivity measurements. The extended portions of the crystals were removed completely and the opposite faces were polished and coated with good quality graphite to obtain a good ohmic contact.

The D.C. electrical conductivity measurements were carried out along both the unique axis (c-) and perpendicular (a- and b-) directions for all the eleven crystals grown using the conventional two-probe technique using a million megohmmeter at various temperatures ranging from 40 to 150°C. The dimensions of the crystals were measured using a travelling microscope (L.C. = 0.001cm). The conductivity (σ) of the crystal was calculated using the relation

$$\sigma = \frac{d}{RA},$$

where R is the measured resistance, d the thickness of the sample crystal and A the area of the face of the crystal in contact with the electrode. Inaccuracy involved in this measurement was within ±4%.

Plots between ln(σ) and 1000/T were found to be very nearly linear. So, the conductivity values can be fitted to the relation

$$\sigma = \sigma_0 \exp \frac{-E}{kT}$$

where E is the activation energy, k the Boltzmann constant T the absolute temperature and σ_0 the parameter depending on the material. Activation energies were estimated using the slopes of the above line plots [E = -(slope)k × 1000]

3. Results and discussion

Scalenohedral morphology was exhibited by all the crystals grown. All the crystals grown were found to be stable colourless and transparent

It was observed that the difference in densities of crystals grown in the same container was very small and negligible Average densities are given in Table 1. The value observed for pure KDP (2.318 g/cc) compares well with that reported in the literature (2.338 g/cc) [14]. For both the impurities considered in the present study, the observed variation of density of KDP crystal caused by the impurities indicates that the impurities have entered into the lattice of KDP crystals Moreover, it can be seen that the density varies further with the increase in impurity concentration of the aqueous solution of KDP used for the growth of crystals.

Table 1. Densities and activation energies

System (impurity in mole%)	Density (g/cc)	Activation energy, a- direction	E(eV) along c direction
a) Pure KDP	2.318	0.538	0.325
b) NaCl added KDP			
0.2	2.305	0.457	0.402
0.4	2.303	0.474	0.522
0.6	2.293	0.484	0.587
0.8	2.290	0.506	0.679
1.0	2.200	0.541	0.376
c) NaBr added KDP			
0.2	2.320	0.608	0.560
0.4	2.324	0.824	0.624
0.6	2.328	0.476	0.564
0.8	2.330	0.431	0.645
1.0	2.332	0.400	0.345

The estimated impurity concentration values are presented in Table 2. In real crystals, concentration of interstitials is expected to be of the order of 10^{15}–10^{20} cm^{-3} *i.e.* up to a maximum of 1% (Here concentration of molecule

is assumed as 10^{22} cm^{-3}). In the present study, the estimated impurity concentration shows that the impurity in the crystal is mainly occupying the interstitial positions.

Table 2. Estimated impurity concentrations.

Impurity concentration in the solution (mole%)	Estimated impurity concentration in the crystal (mole%)	
	For NaCl added KDP	For NaBr added KDP
0.2	0.075	0.125
0.4	0.161	0.276
0.6	0.247	0.427
0.8	0.333	0.579
1.0	0.419	0.729

The σ values obtained along the two directions (a- and b-) perpendicular to the unique axis (c-direction) are, within experimental error, the same. Tables 3-6 provide the σ values for the pure and impurity added KDP crystals. The values of the activation energy, E for pure and impurity added KDP crystals are given in Table 1.

Table 3. D.C. electrical conductivities of NaCl added KDP crystals along a- direction

T (°C)	Conductivity σ (x 10^{-6} mho m^{-1})					
	Pure KDP	1: 0.002	1:0.004	1:0.006	1: 0.008	1: 0.010
40	5.820	9.526	4.944	3.049	1.410	1.225
50	15.114	15.610	8.598	5.146	3.526	2.450
60	22.998	32.630	17.656	16.468	5.641	6.124
70	51.387	55.200	34.095	28.394	9.726	13.123
80	62.399	76.952	61.797	41.174	17.630	18.373
90	174.703	283.286	82.393	72.485	32.055	33.405
100	264.690	334.784	100.899	91.491	58.768	48.993
110	349.650	379.075	152.114	105.563	91.000	76.552
120	472.144	415.800	247.219	211.149	108.495	131.234
130	632.911	460.405	299.580	249.501	128.223	146.972
140	874.126	537.085	380.228	278.164	141.043	183.722
150	1027.740	661.025	494.315	316.656	156.715	204.123

Conductivities obtained in the present study are of the same order with those obtained by previous workers for the KDP crystals (x 10^{-6} mho m^{-1}) [2, 5, 10-12, 15].

It can be seen that for both the impurities considered in the present study, the D.C. electrical conductivity increases with the increase in temperature along both *a*- and *c*-directions. This is similar to that observed by previous authors for their systems. The defect concentration will increase exponentially with temperature and consequently the electrical conduction also increases. The addition of impurity further increases the electrical conduction in the temperature region considered.

Table 4. D.C electrical conductivities of NaCl added KDP crystals along c- direction

T (°C)	Conductivity σ (x 10^{-6} mho m^{-1})					
	Pure KDP	1: 0.002	1:0 004	1 0 006	1: 0 008	1. 0 010
40	54 882	7 944	1 107	0 309	0 097	1 875
50	151 920	14 896	2 604	1 235	0 521	4 395
60	259 940	23 833	4 427	4 325	1 202	7 814
70	395 256	34 047	5 208	6 653	3 126	19 535
80	493.827	42 559	8 049	12 356	7 815	28 130
90	658 761	66.203	15 811	20 593	13.026	41.370
100	898 490	116.822	26.042	33 266	21 124	54 097
110	968 054	150.829	55 340	48.052	31.263	63 935
120	988 142	183 318	76 335	66.533	47 368	70 333
130	1234 560	248 262	92 233	82 372	65 133	72 129
140	1317.520	315 955	110 680	88 253	78 162	74 030
150	2597 410	410 340	170 270	151 745	91 954	78 143

Table 5. D.C electrical conductivities of NaBr added KDP crystals along a- direction

T (°C)	Conductivity σ (x 10^{-6} mho m^{-1})					
	Pure KDP	1 0.002	1 0 004	1 0 006	1 0.008	1 0 010
40	5 820	1.737	1 358	1 332	0 683	0 422
50	15 114	3 257	8.133	4 077	5 592	1 733
60	22.998	7.273	11 638	10 741	10 251	28 889
70	51 387	15 953	27 155	26.997	12 060	30 144
80	62 399	32 570	55 546	48 726	21 581	33 017
90	174 703	55 834	81 466	84.653	29 289	36 684
100	264 690	82 284	116 374	79 911	36.181	42.535
110	349 650	130.276	162 919	95 129	43 935	44 731
120	472 144	200 440	222 222	105 141	51.256	51 358
130	632 911	312 695	349 162	144 759	72 364	55 466
140	874 126	434 216	436.490	169 291	82 008	57.777
150	1027 740	558.347	555.555	195 886	129 483	69 334

For the pure KDP crystal, the σ values are more along *c*-direction than along *a*-direction. Along *a*-direction, the conductivity is less at the minimum (40°C) and maximum (150°C) temperatures for NaBr added KDP crystals than that for NaCl added KDP crystals. However, along *c*-direction, the reverse is true. There is no systematic variation of σ observed with the impurity concentration for both the impurities considered in the present study. However, though it is not highly authentic (some deviations occur at low temperatures along *a*-direction in the case of 0.2 mole% addition of NaCl), it can be stated that the impurity addition leads to reduction of electrical conductivity in KDP crystals when NaCl and NaBr are the impurities. This result is different from that observed by us previously for KDP

Table 6. D.C. electrical conductivities of NaBr added KDP crystals along c- direction.

T (°C)	Conductivity σ (x 10^{-6} mho m^{-1})					
	Pure KDP	1· 0.002	1 0.004	1 0.006	1· 0 008	1. 0.010
40	54.882	2.051	1 679	1.595	0 709	7 098
50	151 920	5.351	1.699	3.637	1 777	11.534
60	259.940	13 674	2.388	10 333	4 575	20.505
70	395.256	30.767	9.302	18.557	9.782	33.554
80	493.827	53.507	14 978	34.972	23.639	43 424
90	658 761	98.454	34.656	58 665	44 324	62.559
100	898.490	164.096	55.233	89 162	78.795	82.021
110	968.054	231 857	80.341	118 662	128.949	108.554
120	988 142	314.268	103 972	189 420	161 186	136 705
130	1234.560	323.834	184 094	259.860	218 198	153 798
140	1317.520	410.341	276 166	336 813	278.080	167.757
150	2597.410	512 821	490.918	378 931	295.508	205 044

crystals added with five ammonium compound impurities [10], potassium compounds (KCl and KNO_3) [11] and organic compounds (urea and thiourea) [12]. In all the earlier systems, the conductivity in KDP crystals increases with the increase in impurity concentration.

It is a known fact that NaCl and NaBr are model ionic substances and they exist as single ions in the crystals. So in all the impurity added systems considered in the present study, the halide ions are also expected to move (in all directions) along with protonic movement (it has already been established that the electrical conduction in KDP crystals is protonic [10]) which may create a complex situation on the electrical conduction of KDP crystals. This may be the reason for the non-observance of systematic variation of conductivity with impurity concentration in the present study. In addition, movement of halide ions in the same direction with that of protons (as they have unlike charges) may be the reason for the reduction of electrical conductivity in the case of impurity (NaCl and NaBr) added KDP crystals.

4. Conclusions

Pure and impurity (NaCl and NaBr) added KDP single crystals were grown and electrical conductivities were measured along both the *a*- and *c*- directions at various temperatures ranging from 40 to 150°C. Density measurement indicates that the impurity molecules have entered into the lattice of KDP crystals. The present study indicates that the conductivity increases with the increase in temperature. Non- observance of systematic variation of conductivity with impurity concentration and observation of reduction in conductivity with the impurity addition in the present study could be explained by considering the complex situation created by the halide impurity ions in the electrical conduction of KDP crystals.

References

[1] K B R Varma, K V Ramanaiah and K V Rao *Bull Mater Sci* **5** 39 (1983)

[2] M Shanmugham, F D Gnanam and P Ramasamy *Indian J Pure Appl Phys.* **23** 82 (1985)

[3] H K Henisch *Crystals in Gels and Liesegang Rings* (Cambridge Cambridge University Press) (1988)

[4] L N Rashkovich *KDP -Family Single Crystals* (New York Adam Hilger) (1991)

[5] K Somasekhara Udupa, P Mohan Rao, Sriramana Atthal A P Bhat and D K Avasthi *Bull Mater Sci* **20** 1069 (1997)

[6] V A Kuznetsov, T M Okhrimenko and M Rat *J Cryst Growth* **193** 164 (1998)

[7] T H Freeda and C Mahadevan *Pramana - J Phys* 57 82[illegible] (2001)

[8] A D Q Livingsta, T Mary Jeeva, C Mahadevan and C Balasingh *Indian J. Phys* **75A** 241 (2001)

[9] R W G Wyckoff *Crystal Structures* 2nd edn Vol 3 (New York Interscience) p 160 (1960)

[10] T H Freeda and C Mahadevan *Bull. Mater Sci* 23 [illegible] (2000)

[11] J Albin Sancta, A Gnana Sutha, T H Freeda, C Mahadevan and C Balasingh *Indian J Phys.* **75A** 245 (2001)

[12] M Priya, C M Padma, T H Freeda, C Mahadevan and C Balasingh *Bull. Mater Sci* **24** 511 (2001)

[13] R Krishnaswamy *Crystals growth and Characterization of Mixed Crystals and Doped Crystals, Proceedings of the Second National Seminar on Crystal Growth* (Chennai Anna University) p 58 (1984)

[14] John A Dean (Edn) *Lange's Handbook of Chemistry* XII edn (New York: McGraw-Hill) (1979)

[15] B Shanthini, C Anitha, C Mahadevan and C Balasingh *Indian J. Phys.* **73A** 805 (1999)